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ATTORNEY'S DOCKET NUMBER

FA-1068

**TRANSMITTAL LETTER TO THE UNITED STATES  
DESIGNATED/ELECTED OFFICE (DO/EO/US)  
CONCERNING A FILING UNDER 35 U.S.C. 371**

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR)

**10/089810**

INTERNATIONAL APPLICATION NO.

**PCT/EP00/09387**

INTERNATIONAL FILING DATE

**26 SEPTEMBER 2000 (26.09.00)**

PRIORITY DATE CLAIMED

**2 OCTOBER 1999 (02.10.99)**

TITLE OF INVENTION

**METHOD FOR PRODUCING BASE VARNISH/CLEAR VARNISH-TWO-COAT VARNISHES AND/OR TRANSPARENT SEALING LAYERS**

APPLICANT(S) FOR DO/EO/US

**BRANDT, Lutz et al.**

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This is an express request to being national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b)) and PCT Articles 22 and 39(1).
4. ☒ A proper Demand for International Preliminary Examination was made by the 19<sup>th</sup> month from the earliest claimed priority date.
5. ☒ A copy of the International Application was filed (35 U.S.C. 371 (c) (2))
  - a. ☒ is transmitted herewith (required only if not transmitted by the International Bureau.
  - b. ☐ has been transmitted by the International Bureau.
  - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US)
6. ☒ A translation of the International Application into English (35 U.S.C. 371 (c) (2)).
7. ☒ A copy of the International Search Report (PCT/ISA/210).
8. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371 (c) (3))
  - a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
  - b. ☐ have been transmitted by the International Bureau.
  - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
  - d. ☒ have not been made and will not be made.
9. ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371 (c)(3)).
10. ☐ An oath or declaration of the inventor(s) (35 U.S.C. 371 (c)(4)).
11. ☒ A copy of the International Preliminary Examination Report (PCT/IPEA/409)
12. ☐ A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371 (c)(5)).

**Items 13 to 18 below concern document(s) or information included :**

13. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
14. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
15. ☒ A **FIRST** preliminary amendment.  
A **SECOND** or **SUBSEQUENT** preliminary amendment.
16. ☐ A substitute specification.
17. ☒ A change of power of attorney and/or address letter.
18. ☒ Certificate of Mailing by Express Mail.
19. ☐ Other items or information:

**17. General Power of Attorney****18. Express Mailing Label No.: EJ376013461US**

APPLICATION NO. (IF KNOWN, SEE 37 CFR) <b>10/089810</b>		INTERNATIONAL APPLICATION NO. <b>PCT/EP00/09387</b>		ATTORNEY'S DOCKET NUMBER <b>FA-1068</b>	
20. The following fees are submitted  <b>BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) – (5)) :</b> <input checked="" type="checkbox"/> Search Report has been prepared by the EPO or JPO \$890.00 <input type="checkbox"/> International preliminary examination fee paid to USPTO (37 CFR 1.482) \$710.00 <input type="checkbox"/> No international preliminary examination fee paid to USPTO (37 CFR 1.482) but international search fee paid to USPTO (37 CFR 1.445(a)(2)) \$740.00 <input type="checkbox"/> Neither international preliminary examination fee paid to USPTO (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO \$1,040.00 <input type="checkbox"/> International preliminary examination fee paid to USPTO (37 CFR 1.482) And all claims satisfied provisions of PCT Article 33(2)-(4) \$ 100.00				<b>CALCULATIONS PTO USE ONLY</b>	
<b>ENTER APPROPRIATE BASIC FEE AMOUNT =</b>				<b>\$890.00</b>	
Surcharge of <b>\$130.00</b> for furnishing the oath or declaration later than months from the earliest claimed priority date (37 CFR 1.492 (e)). <input type="checkbox"/> 20 <input checked="" type="checkbox"/> 30				<b>\$130.00</b>	
<b>CLAIMS</b>	<b>NUMBER FILED</b>	<b>NUMBER EXTRA</b>	<b>RATE</b>		
Total Claims	<b>19 - 20 =</b>	<b>0 x</b>	<b>\$18.00</b>	<b>\$0.00</b>	
Independent Claims	<b>2 - 3 =</b>	<b>0 x</b>	<b>\$84.00</b>	<b>\$0.00</b>	
Multiple Dependent Claims (check if applicable)			<input checked="" type="checkbox"/>	<b>\$280.00</b>	
<b>TOTAL OF ABOVE CALCULATIONS =</b>				<b>\$280.00</b>	
Reduction of ½ for filing by small entity, if applicable. Verified Small Entity Statement must also be filed (Note 37 CFR 1.9, 1.27, 1.28) (check if applicable). <input type="checkbox"/>				<b>\$0.00</b>	
<b>SUBTOTAL =</b>				<b>\$280.00</b>	
Processing Fee of <b>\$130.00</b> for furnishing the English translation later than months from the earliest claimed priority date (37 CFR 1.492 (f)). <input type="checkbox"/> 20 <input type="checkbox"/> 30				<b>\$0.00</b>	
<b>TOTAL NATIONAL FEE =</b>				<b>\$1,300.00</b>	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31) (check if applicable). <input type="checkbox"/>				<b>\$0.00</b>	
<b>TOTAL FEES ENCLOSED =</b>				<b>\$1,300.00</b>	
				Amount to be : refunded	\$
				Charged	\$
<input type="checkbox"/> A check in the amount of _____ to cover the above fees enclosed. <input checked="" type="checkbox"/> Please charge my Deposit Account No. <b>04-1928</b> in the amount of <b>\$1,300.00</b> to cover the above fees. <input checked="" type="checkbox"/> The Commissioner is hereby authorized to charge any fees which may be required, or credit any overpayment to Deposit Account No. <b>04-1928</b> a duplicate copy of this sheet is enclosed.					
<b>NOTE : Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (CFR 1.37(a) or (b)) must be filed and granted to restore the application to pending status.</b>					
<b>SEND ALL CORRESPONDENCE TO:</b>					
<b>BENJAMIN, Steven C.</b> <b>E. I. DU PONT DE NEMOURS AND COMPANY</b> Legal Patent Records Center 4417 Lancaster Pike Wilmington, Delaware 19805 United States of America			SIGNATURE _____ <b>BENJAMIN, STEVEN C.</b> NAME _____ <b>36,087</b> REGISTRATION NUMBER _____ <b>April 1, 2002</b> DATE _____		

PATENT  
IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant:

LUTZ BRANDT, ET AL.

Case No: FA1068

Application No: UNKNOWN

Group Art Unit: UNKNOWN

Filed: CONCURRENTLY HEREWITH

Examiner: UNKNOWN

For: METHOD FOR PRODUCING BASE  
VARNISH/CLEAR VARNISH-TWO-COAT  
VARNISHES AND/OR TRANSPARENT  
SEALING LAYERS

Assistant Commissioner for Patents  
Washington, D.C. 20231

Sir:

**PRELIMINARY AMENDMENT**

It is respectfully requested that the Examiner enter the amendments below prior to examining the above-identified application on its merits. Please amend the application as follows:

**IN THE SPECIFICATION:**

Please replace the paragraph beginning at page 1, line 6, with the following rewritten paragraph:

**Background of the Invention**

The invention relates to a process for the production of transparent finishing coats, in particular the clear lacquer coats of decorative base lacquer/clear lacquer two-coat lacquers and/or of transparent sealing coats on the outer finishing coat of lacquered surfaces of a substrate using radiation-curable coating agents, and the substrates thus obtained.

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Please replace the paragraph beginning at page 1, line 12, with the following rewritten paragraph:

Processes for the production of multi-coat lacquers by the application of a clear lacquer coat of a radiation-curable coating agent to a pigmented base lacquer coat and subsequent curing of the clear lacquer coat by the action of actinic radiation are known from EP-A-0 540 884 and WO 98 40 171. Both parent documents disclose clear lacquer compositions including those containing urethane (meth)acrylates.

Please replace the paragraph beginning at page 1, line 18, with the following rewritten paragraph:

The clear lacquer formulations according to EP-A-0 540 884 and WO 98 40-171 are suitable for the production of scratch-resistant base lacquer/clear lacquer two-coat lacquers, however the flexibility of the two-coat lacquers needs to be improved. The clear lacquers referred to in the examples of EP-A-0 540 884 and WO 98 40 171 have relatively high contents of low or non-volatile reaction thinners which, after application of the clear lacquers, can lead to an undesirable partial dissolution of the base lacquer coats resulting in deviations in colour or effect.

Please replace the paragraph beginning at page 1, line 26, with the following rewritten paragraph:

A process for the production of multi-coat lacquers by the application of a heat-cured clear lacquer coat to a pigmented base lacquer coat, subsequent heat curing and application of a further clear lacquer coat based on radiation curable coating agents, and subsequent curing of the second clear lacquer coat by the action of actinic radiation, is known from EP-A-0 568 967.

Please replace the paragraph beginning at page 2, line 1, with the following rewritten paragraph:

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The demands for scratch resistance of vehicle lacquers are constantly increasing.

Multi-coat lacquers produced according to the examples of EP-A-0 568 967 are scratch-resistant, but very brittle.

Please replace the paragraph beginning at page 2, line 13, with the following rewritten paragraph:

The object can be achieved in that a clear lacquer coat, curable by radical polymerisation, is applied to a previously applied colour and/or effect-providing base lacquer coat and/or a transparent coating agent coat is applied to the outer finishing coat of a lacquered substrate surface and this is cured by the action of high-energy radiation, a transparent coating agent being used to apply the outer clear lacquer finishing coat and/or sealing coat, which contains as the substantial or only constituent to its resin solid, an aliphatic urethane (meth)acrylate.

Please replace the paragraph beginning at page 2, line 19, with the following rewritten paragraph:

### **Summary of the Invention**

The invention therefore provides a process for the production of a base lacquer/clear lacquer two-coat lacquer and/or a transparent sealing coat on the outer finishing coat of a lacquered substrate surface, in which a clear lacquer coat curable by radical polymerisation is applied to a previously applied colour and/or effect-providing base lacquer coat and/or a transparent coating agent coat is applied to the outer finishing coat of a lacquered substrate surface and cured by the action of high-energy radiation, characterised in that to apply the outer clear lacquer coat and/or sealing coat, a transparent coating agent is used of which the resin solid consists of:

Please replace the paragraph beginning at page 3, line 15, with the following rewritten paragraph:

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## Detailed Description of the Invention

The resin solid of the coating agents used in the process according to the invention to produce the clear lacquer top coat and/or sealing coat consists of binder (component I) and optionally present reactive thinners (component II) in the weight ratio given above. The term “resin solid” does not take account of the fact that component I or, in particular, component II, may contain volatile portions, for example portions, which are volatile during application or curing of the clear lacquer top coat and/or sealing coat, and thus does not exclude such portions.

Please replace the paragraph beginning at page 7, line 26 through page 8, line 4, with the following rewritten paragraph:

The resin solid of the clear lacquer coating agents and/or sealing coating agents can contain as component II, 0 to 30, more preferably 0 to 10 wt.% and even more preferably 0 to 5 wt.% of one or more reactive thinners having radically polymerisable olefinic unsaturated groups with calculated molar masses of less than 500 each. It is particularly preferred, if the selected proportion of reactive thinners in the resin solid is low and in particular if there is no reactive thinner in the clear lacquer coating agent and/or sealing coating agent. The reactive thinners of component II are low-molecular compounds, which can be mono-, di- or polyunsaturated. The reactive thinners can be volatile, slow-evaporating or non-volatile compounds. Examples of reactive thinners are: (meth)acrylic acid and its esters, maleic acid and its semi-esters, vinyl acetate, vinyl ether, substituted vinyl ureas, ethylene- and propylene glycol di(meth) acrylate, 1,3- and 1,4-butanediol di(meth) acrylate, vinyl(meth)acrylate, ally(meth)acrylate, glycerine tri-, di- and mono(meth)acrylate, trimethylol propane tri-, di- and mono(meth)acrylate, styrene, vinyl toluene, divinyl

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benzene, pentaerythrite tri-, and tetra(meth)acrylate, di- and tripropylene glycol di(meth)acrylate, hexandediol di(meth)acrylate and mixtures thereof.

Please replace the paragraph beginning at page 8, line 19 with the following rewritten paragraph:

The clear lacquer coating agents ad/or sealing coating agents used in the process according to the invention can contain thermally activable radical initiators. Examples of thermolabile radical initiators are: organic peroxides, organic azo compounds or C-C splitting initiators, such as dialkyl peroxides, peroxocarboxylic acids, peroxodicarbonates, peroxide esters, hydroperoxides, ketone peroxides, azo dinitriles or benzopinacolsilylether. They are preferably used in quantities of 0.1 to 5 wt. % in relation to the resin solid.

Please replace the paragraph beginning at page 16, line 24, with the following rewritten paragraph:

The resin solutions from examples 1a-e and 1h-l are each thinned with butyl acetate to a solids content of 60 wt.% 97 parts by weight of each solution is mixed with 0.1 parts by weight of a radically polymerisable silicon levelling additive, 1 part by weight of a light protection agent (HALS, hindered amine light stabilizer) 0.5 parts by weight of a UV absorber based on benzo triazol, 1 part by weight of a photo-initiator from the alpha hydroxy ketones group and 0.4 parts by weight of a photo-initiator from the acylphosphine oxides group.

#### **IN THE CLAIMS:**

Please CANCEL claims 1-9 without prejudice or disclaimer of the subject matter thereof.

Please ADD the following new claims:

Claim 10. A process for producing a clear lacquer coating in a base lacquer/clear lacquer two-coat lacquering system, comprising the steps of:

- a) applying a base lacquer coating selected from the group consisting of a color-providing base lacquer coating and an effect-providing base lacquer coating to a substrate;

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- b) applying the clear lacquer coating onto the base lacquer coating as a top coating, said clear lacquer coating being curable by radical polymerization; and
- c) curing said clear lacquer coating with high-energy radiation;

wherein the clear lacquer coating comprises a resin solid consisting of:

- I. 70 to 100 wt.% of at least one radically polymerizable polymer selected from the group consisting of oligomers and prepolymers, wherein said polymers have at least one olefinically unsaturated group; and
- II. 0 to 30 wt.% of at least one radically polymerizable reactive thinner having olefinically unsaturated groups and having a calculated molar mass of less than 500;

wherein 75 to 100 wt.% of component I is an aliphatic urethane (meth)acrylate having an average (meth)acryloyl functionality of 3 to 4.5 and a calculated molecular mass of at least 826;

wherein said aliphatic urethane (meth)acrylate is formed by reacting an acyclic aliphatic diisocyanate having 8 C atoms with at least one low-molecular aliphatic compound, wherein said low-molecular aliphatic compound has at least one hydroxy group and at least one (meth)acryloyl group, and optionally with at least one low-molecular aliphatic hydroxy reactant selected from the group consisting of diols and polyols; and

wherein 0 to 25 wt.% of component I is a radically polymerizable member selected from the group consisting of polymers and oligomers, wherein said radically polymerizable member contains radically polymerizable double bonds, said radically polymerizable member being different from the aliphatic urethane (meth)acrylate of component I.

Claim 11. The process according to claim 10 wherein the aliphatic urethane (meth)acrylate is formed by reacting polyisocyanates based on acyclic aliphatic diisocyanates having 8 C atoms, wherein the polyisocyanates contain heteroatom groups linking isocyanate groups together in said polyisocyanates, with at least one low-molecular aliphatic compound, wherein said low-molecular aliphatic compound





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wherein said aliphatic urethane (meth)acrylate is formed by reacting an acyclic aliphatic diisocyanate having 8 C atoms with at least one low-molecular aliphatic compound, wherein said low-molecular aliphatic compound has at least one hydroxy group and at least one (meth)acryloyl group, and optionally with at least one low-molecular aliphatic hydroxyl reactant selected from the group consisting of diols and polyols and

wherein 0 to 25 wt.% of component I is a radically polymerizable member selected from the group consisting of polymers and oligomers, wherein said radically polymerizable member contains radically polymerizable double bonds, said radically polymerisable member being different from the aliphatic urethane (meth)acrylate of component I.

Claim 14. The process according to claim 13 wherein the aliphatic urethane (meth)acrylate is formed by reacting polyisocyanates based on acyclic aliphatic diisocyanates having 8 C atoms, wherein the polyisocyanates contain heteroatom groups linking isocyanate groups together in said polyisocyanates, with at least one low-molecular aliphatic compound, wherein said low-molecular aliphatic compound has at least one hydroxy group and at least one (meth)acryloyl group, and optionally with at least one low-molecular aliphatic hydroxyl reactant selected from the group consisting of diols and polyols.

Claim 15. The process according to claim 13 wherein the transparent sealing coat comprises a resin solid consisting of:

- I. 90 to 100 wt.% of at least one radically polymerizable polymer selected from the group consisting of oligomers and prepolymers, wherein said polymers have at least one olefinically unsaturated group; and
- II. 0 to 10 wt.% of at least one radically polymerizable reactive thinner having olefinically unsaturated groups and having a calculated molar mass of less than 500.

Claim 16. The process according to claim 10 or 13, wherein the acyclic aliphatic diisocyanate having 8 C atoms is selected from the group consisting of methyl pentane diisocyanate and hexane diisocyanate.

Claim 17. The process according to claim 11 or 14, wherein the polyisocyanates are selected from the group consisting of polyisocyanates with carbodiimide groups, polyisocyanates with allophanate groups, polyisocyanates with isocyanurate groups, polyisocyanates with uretdione groups, and polyisocyanates with biuret groups.

Claim 18. The process according to claim 11 or 14, wherein the polyisocyanates are selected from the groups consisting of tris-(6-isocyanatohexyl)-biuret and isocyanurate derived from hexane diisocyanate.

Claim 19. The process according to claim 13 wherein the transparent sealing coat is applied in step (a) to an outer lacquer coating selected from the group consisting of a single-coat finishing lacquer coat, an outer finishing lacquer coat, and an outer clear lacquer coat.

Claim 20. A substrate coated according to the process of claim 10.

Claim 21. A substrate coated according to the process of claim 13.

Claim 22. The substrate according to claim 20 or 21 wherein said substrate is a motor vehicle or part thereof.

Claim 23. The process according to claim 13 wherein said transparent sealing coat is applied in step (a) to areas of the outer lacquer coating particularly susceptible to scratching.

Claim 24. The process according to claim 23 wherein said transparent sealing coat is applied to areas of a motor vehicle selected from the group consisting of areas near locks, areas near door handles, areas near door entries, loading edges, roof, and rear end of said motor vehicle.

#### **IN THE ABSTRACT**

Please replace the Abstract beginning at page 25 line 6, with the following rewritten Abstract:

Process for the production of a base lacquer/clear lacquer two-coat lacquer and/or a transparent sealing coat on the outer finishing coat of a lacquered surface of a

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substrate by application of a transparent coating agent curable by radical polymerization and curing by the action of high-energy radiation, a transparent coating agent being used, of which the resin solid consists of:

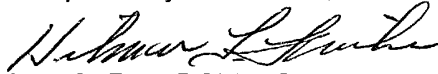
- I. 70 to 100 wt.% radically polymerisable oligo- and/or prepolymers having olefinic groups
  - II. 0 to 30 wt.% radically polymerisable reactive thinners having olefinic groups, with calculated molar masses of less than 500 each,
- wherein 75 to 100 wt.% of component 1 is an aliphatic urethane (meth)acrylate with an average (meth)acryloyl functionality of 3 to 4.5 per molecule and a calculated molecular mass of at least 826, which can be obtained by reacting acyclic aliphatic diisocyanates with 8 C atoms and/or polyisocyanates derived from such diisocyanates with low-molecular aliphatic compounds, which have one or more hydroxyl groups and at the same time one or more (meth)acryloyl groups.

**REMARKS**

In the specification, the section headings have been inserted and on page 2, line 2, the patent number was corrected to correspond with the patent number shown on page 1, lines 29 and 30. Minor amendments have been made to the specification and to the Abstract.

Claims 1-9 have been cancelled. Claims 10-24 are submitted herewith in a format acceptable to the United States Patent and Trademark Office. If the Examiner has questions regarding the application or the contents of this Preliminary Amendment, the Examiner is invited to contact the undersigned at the number provided below.

Respectfully submitted,



**HILMAR L. FRICKE**  
ATTORNEY FOR APPLICANTS  
REGISTRATION NO. 22,384  
TELEPHONE: (302) 992-6058  
FACSIMILE: (302) 658-1192

DATE: MARCH 27, 2002

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**VERSION WITH MARKINGS TO SHOW CHANGES MADE**

In showing the changes, the material to be deleted is shown as a strike through and the material to be inserted is underlined.

**IN THE SPECIFICATION**

Paragraph beginning at page 1, line 6, has been amended as follows:

**Background of the Invention**

The invention relates to a process for the production of transparent finishing coats, in particular the clear lacquer coats of decorative base lacquer/clear lacquer two-coat lacquers and/or of transparent sealing coats on the outer finishing coat of lacquered surfaces of a substrate using radiation-cured curable coating agents, and the substrates thus obtained.

Paragraph beginning at page 1, line 12, has been amended as follows:

Processes for the production of multi-coat lacquers by the application of a clear lacquer coat of a radiation-cured curable coating agent to a pigmented base lacquer coat and subsequent curing of the clear lacquer coat by the action of actinic radiation are known from EP-A-0 540 884 and WO 98 40 171. Both parent documents disclose clear lacquer compositions including those containing urethane (meth)acrylates.

Paragraph beginning at page 1, line 18, has been amended as follows:

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The clear lacquer formulations according to EP-A-0 540 884 and WO 98 40-171 are suitable for the production of scratch-resistant base lacquer/clear lacquer two-coat lacquers, however the flexibility of the two-coat lacquers needs to be improved. The clear lacquers referred to in the examples of EP-A-0 540 884 and WO 98 40 171 have relatively high contents of heavy low or non-volatile reaction thinners which, after application of the clear lacquers, can lead to an undesirable partial dissolution of the base lacquer coats resulting in deviations in colour or effect.

Paragraph beginning on page 1, line 26, has been amended as follows:

A process for the production of multi-coat lacquers by the application of a heat-cured clear lacquer coat to a pigmented base lacquer coat, subsequent heat curing and application of a further clear lacquer coat based on radiation-cured curable coating agents, and subsequent curing of the second clear lacquer coat by the action of actinic radiation, is known from EP-A-0 568 967.

Paragraph beginning at page 2, line 1, has been amended as follows:

The demands for scratch resistance of vehicle lacquers are constantly increasing. Multi-coat lacquers produced according to the examples of EP-A-0 568 697 967 are scratch-resistant, but very brittle.

Paragraph beginning at page 2, line 13, has been amended as follows:

Please replace the paragraph beginning at page 2, line 13, with the following rewritten paragraph:







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The clear lacquer coating agents ad/or sealing coating agents used in the process according to the invention can contain thermally ~~activated~~ activable radical initiators. Examples of thermolabile radical initiators are: organic peroxides, organic azo compounds or C-C splitting initiators, such as dialkyl peroxides, peroxocarboxylic acids, peroxodicarbonates, peroxide esters, hydroperoxides, ketone peroxides, azo dinitriles or benzopinacolsilylether. They are preferably used in quantities of 0.1 to 5 wt. % in relation to the resin solid.

Paragraph beginning at page 16, line 24, has been amended as follows:

The resin solutions from examples 1a-e and 1h-l are each thinned with butyl acetate to a solids content of 60 wt.% 97 parts by weight of each solution is mixed with 0.1 parts by weight of a radically polymerisable silicon levelling additive, 1 part by weight of a light protection agent (HALS, hindered amine light stabilizer) 0.5 parts by weight of a UV absorber based on ~~benzene~~ benzo triazol, 1 part by weight of a photo-initiator from the alpha hydroxy ketones group and 0.4 parts by weight of a photo-initiator from the acylphosphine oxides group.

### **IN THE CLAIMS**

Claims 1-9 have been canceled.

Claims 10-24 have been added.

**IN THE ABSTRACT**

Abstract beginning at page 25 line 6, has been amended as follows:

Process for the production of a base lacquer/clear lacquer two-coat lacquer and/or a transparent sealing coat on the outer finishing coat of a lacquered surface of a substrate by application of a transparent coating agent ~~cured~~ curable by radical polymerization and curing by the action of high-energy radiation, a transparent coating agent being used, of which the resin solid consists of:

- I. 70 to 100 wt.% radically polymerisable oligo- and/or prepolymers having olefinic groups
  - II. 0 to 30 wt.% radically polymerisable reactive thinners having olefinic groups, with calculated molar masses of less than 500 each,
- wherein 75 to 100 wt.% of component 1 is an aliphatic urethane (meth)acrylate with an average (meth)acryloyl functionality of 3 to 4.5 per molecule and a calculated molecular mass of at least 826, which can be obtained by reacting acyclic aliphatic diisocyanates with 8 C atoms and/or polyisocyanates derived from such diisocyanates with low-molecular aliphatic compounds, which have one or more hydroxyl groups and at the same time one or more (meth)acryloyl groups.

E. I. du Pont de Nemours and Company

5 Method for producing base varnish/clear varnish-two-coat varnishes  
and/or transparent sealing layers

The invention relates to a process for the production of transparent finishing coats, in particular the clear lacquer coats of decorative base lacquer/clear lacquer two-coat lacquers and/or of transparent sealing coats on the outer finishing coat of lacquered surfaces of a  
10 substrate using radiation-cured coating agents, and the substrates thus obtained.

Processes for the production of multi-coat lacquers by the application of a clear lacquer coat of a radiation-cured coating agent to a pigmented base lacquer coat and subsequent curing of the clear lacquer coat by the action of actinic radiation are known from EP-A-0 540 884 and  
15 WO 98 40 171. Both patent documents disclose clear lacquer compositions including those containing urethane (meth)acrylate.

The clear lacquer formulations according to EP-A-0 540 884 and WO 98 40 171 are suitable for the production of scratch-resistant base lacquer/clear lacquer two-coat lacquers, however  
20 the flexibility of the two-coat lacquers needs to be improved. The clear lacquers referred to in the examples of EP-A-0 540 884 and WO 98 40 171 have relatively high contents of heavy or non-volatile reactive thinners which, after application of the clear lacquers, can lead to an undesirable partial dissolution of the base lacquer coats resulting in deviations in colour or effect.

25

A process for the production of multi-coat lacquers by the application of a heat-cured clear lacquer coat to a pigmented base lacquer coat, subsequent heat curing and application of a further clear lacquer coat based on radiation-cured coating agents, and subsequent curing of the second clear lacquer coat by the action of actinic radiation, is known from EP-A-0 568  
30 967.

The demands for scratch resistance of vehicle lacquers are constantly increasing. Multi-coat lacquers produced according to the examples of EP-A-0 568 697 are scratch-resistant, but very brittle.

- 5 The object of the invention is to provide a process for the production of transparent finishing coats, in particular in the context of base lacquer/clear lacquer two-coat lacquers and/or transparent sealing coats on the outer finishing coat of a lacquered substrate surface, the outer, clear lacquer coat and/or sealing coat having good flexibility as well as outstanding scratch-resistance. The base lacquer/clear lacquer two-coat lacquers and/or sealing coats  
10 should be suitable for use as vehicle lacquers. Colour and effect deviations caused by the partial dissolution of the base lacquer coats by the clear lacquer should not arise.

The object can be achieved in that a clear lacquer coat, cured by radical polymerisation, is applied to a previously applied colour and/or effect-providing base lacquer coat and/or a  
15 transparent coating agent coat is applied to the outer finishing coat of a lacquered substrate surface and this is cured by the action of high-energy radiation, a transparent coating agent being used to apply the outer clear lacquer finishing coat and/or sealing coat, which contains as the substantial or only constituent of its resin solid, an aliphatic urethane (meth)acrylate. The invention therefore provides a process for the production of a base lacquer/clear lacquer  
20 two-coat lacquer and/or a transparent sealing coat on the outer finishing coat of a lacquered substrate surface, in which a clear lacquer coat cured by radical polymerisation is applied to a previously applied colour and/or effect-providing base lacquer coat and/or a transparent coating agent coat is applied to the outer finishing coat of a lacquered substrate surface and cured by the action of high-energy radiation, characterised in that to apply the outer clear  
25 lacquer coat and/or sealing coat, a transparent coating agent is used, of which the resin solid consists of:

1. 70 to 100 wt.%, preferably 90 to 100 wt.% of one or more radically polymerisable oligo- and/or prepolymers having olefinically unsaturated groups and

II. 0 to 30 wt.%, preferably 0 to 10 wt.% of one or more radically polymerisable reactive thinners having olefinically unsaturated groups, with calculated molar masses of less than 500 each

5 wherein 75 to 100 wt.% of component I is an aliphatic urethane (meth)acrylate with an average (meth)acryloyl functionality of 3 to 4.5 per molecule and a calculated molecular mass of at least 826, which can be obtained by reacting acyclic aliphatic diisocyanates with 8 C atoms and/or polyisocyanates derived from such diisocyanates with one or more low-molecular aliphatic compounds, which have one or more hydroxyl groups and at the same  
10 time one or more (meth)acryloyl groups, and optionally with one or more low-molecular aliphatic diols and/or polyols.

Here (meth)acryl is understood to mean acryl and/or methacryl.

15 The resin solid of the coating agents used in the process according to the invention to produce the clear lacquer top coat and/or sealing coat consists of binder (component I) and optionally present reactive thinners (component II) in the weight ratio given above. The term "resin solid" does not take account of the fact that component I or, in particular, component II, may contain volatile portions, for example portions, which are volatile during application  
20 or curing of the clear lacquer top coat and/or sealing coat, and thus does not exclude such portions.

It is essential to the invention, that up to 75 to 100 wt.%, preferably 90 to 100 wt.%, in particular 100 wt.% of component I consists of an aliphatic urethane (meth)acrylate with an  
25 average (meth)acryloyl functionality of 3 to 4.5 per molecule, preferably over three and under 4, and a calculated molecular mass of at least 826, for example up to 2500, the aliphatic urethane (meth)acrylate being obtainable by reacting an acyclic aliphatic diisocyanate with 8 C atoms and/or polyisocyanates based on such diisocyanates with one or more low-molecular aliphatic compounds, which have one or more hydroxyl groups and at  
30 the same time one or more (meth)acryloyl groups, and also optionally with one or more low-molecular aliphatic diols and/or polyols.

If the (meth)acryloyl functionality of the aliphatic urethane (meth)acrylate falls short of the average of 3 per molecule, the scratch-resistance of the clear lacquer top coat and/or sealing coat produced by the process according to the invention is not satisfactory, whilst its flexibility fulfils the requirements. If the aliphatic urethane (meth)acrylate has an excess (meth)acryloyl functionality of an average of over 4.5 per molecule, both the scratch resistance and flexibility of the clear lacquer top coat and/or sealing coat produced by the process according to the invention are unsatisfactory. Surprisingly, the optimum combination of scratch resistance and flexibility of the clear lacquer top coat and/or sealing coat produced by the process according to the invention appears to be achieved at an average (meth)acryloyl functionality of the aliphatic urethane (meth)acrylate in the range 3 to 4.5 per molecule.

The use of the aliphatic urethane (meth)acrylate defined above makes it possible to formulate clear lacquer coating agents and/or sealing coating agents with a low content of, or without, reactive thinners (component II) in the resin solid. A partial dissolution of base lacquer coats by the clear lacquer coating agents used in the process according to the invention can thus be minimised or virtually eliminated.

The aliphatic urethane (meth)acrylate of component I can be produced by reacting acyclic aliphatic diisocyanates with 8 C atoms and/or polyisocyanates based on such diisocyanates, with one or more low-molecular aliphatic compounds, which have one or more hydroxyl groups and at the same time one or more (meth)acryloyl groups, and also optionally with one or more low-molecular aliphatic diols and/or polyols. Low-molecular aliphatic diols and/or polyols are preferably also used for the production of the aliphatic urethane (meth)acrylates. The stoichiometric ratio of isocyanates, low-molecular aliphatic compounds, which have one or more hydroxyl groups and at the same time one or more (meth)acryloyl groups, and low-molecular aliphatic diols and/or polyols which are preferably also used, is selected in such a way that the aliphatic urethane (meth)acrylate has an average (meth)acryloyl functionality of 3 to 4.5, preferably over 3 and under 4, per molecule and a calculated molecular mass of at least 826, for example up to 2500, preferably

under 2000. With the preferred additional use of low-molecular aliphatic diols and/or polyols for the production of the aliphatic urethane (meth)acrylate of component I, the ratio of hydroxyl equivalents of the low-molecular aliphatic diols and/or polyols to the hydroxyl equivalents of the low-molecular aliphatic compounds, which have one or more hydroxyl groups and at the same time one or more (meth)acryloyl groups is, for example, preferably 0.05:1 to 0.5:1.

The conversion to aliphatic urethane (meth)acrylate can take place in a single synthesis step. If, as is preferred, low-molecular aliphatic diols and/or polyols are also used for the synthesis of the aliphatic urethane (meth)acrylate, production in several successive stages is preferred, for example by first producing, in one or more synthesis steps, from di- or polyisocyanate and low-molecular aliphatic diol(s) and/or polyols, a urethane prepolymer having isocyanate groups with an isocyanate content in relation to the solid of 10 to 20 wt.% for example, (calculated as NCO, formula weight 42), which is then reacted with one or more low-molecular aliphatic compounds, which have one or more hydroxyl groups and at the same time one or more (meth)acryloyl groups, to form the aliphatic urethane (meth)acrylate. The same applies where, in addition to low-molecular aliphatic compounds, which have a hydroxyl group and at the same time one or more (meth)acryloyl groups, low-molecular aliphatic compounds, which have several hydroxyl groups and at the same time one or more (meth)acryloyl groups are used for synthesis of the aliphatic urethane (meth)acrylate.

The aliphatic urethane (meth)acrylate can be produced without solvent in the melt, or in the presence of inert solvents such as e.g. xylene, butylacetate or N-methylpyrrolidone, at temperatures of 20 to 80°C for example. The solvents can then be removed until the desired content is obtained, for example by distillation in a vacuum.

The di- or polyisocyanates used for synthesis of the aliphatic urethane (meth)acrylates are acyclic aliphatic diisocyanates with 8 C atoms such as methylpentane diisocyanate (MPDI) or hexane diisocyanate (HDI), and polyisocyanates preferably based on these diisocyanates, which contain heteroatoms in the group linking the isocyanate groups. Examples of these are



polyisocyanates having carbodiimide groups, allophanate groups, isocyanurate groups, uretdione groups and/or biuret groups, based on acyclic, aliphatic diisocyanates with 8 C atoms, such as e.g. MPDI and/or HDI. HDI-based polyisocyanates are preferred. The HDI-based polyisocyanates known in lacquer technology, such as tris-(6-isocyanatohexyl)-biuret and the isocyanurate derived from HDI are preferred in particular.

The low-molecular aliphatic compounds used for the production of the aliphatic urethane (meth)acrylate, which have one or more hydroxyl groups and at the same time one or more (meth)acryloyl groups are, for example, compounds from the empirical formula of which a molecular weight range of 116 to 340, for example, is calculated. They can be cycloaliphatic, but preferably acyclic aliphatic, compounds, which carry one or more, for example two or three hydroxyl groups and at the same time, one or more, for example two or three (meth)acryloyl groups as substituents. Low-molecular aliphatic compounds, which each carry only one hydroxyl group and only one (meth)acryloyl group are preferred. Examples are pentaerythrite tri-, di-, and mono(meth)acrylate, glycerine di- and mono(meth)acrylate, trimethylol propane di- and mono(meth)acrylate. Examples of the preferred low-molecular aliphatic compounds having only one hydroxyl and only one (meth)acryloyl group per molecule are hydroxyalkyl(meth)acrylates such as e.g. hydroxyethyl(meth)acrylate, the isomeric hydroxypropyl(meth)acrylates, the isomeric hydroxybutyl(meth)acrylates, but also adducts of glycidyl(meth)acrylate and aliphatic monocarboxylic acids or adducts of (meth)acrylic acid and saturated monoepoxide compounds such as versatic acid glycidyl ester.

The low-molecular aliphatic diols and/or polyols preferably also used for the production of the aliphatic urethane (meth)acrylate are, for example, compounds from the empirical formula of which a molecular weight range of 62 to 236, for example, is calculated. They can be cycloaliphatic, but preferably acyclic aliphatic, compounds, which carry two or more, for example up to four hydroxyl groups as substituents. Examples of polyols are pentaerythrite, trimethylol propane and glycerine. Examples of diols are ethylene glycol, propylene glycol, butane diol, pentane diol, hexane diol, neopentyl glycol, butylethylpropane diol, ester diol 204 (pivalyl pivalate), cyclohexane diol, cyclohexane dimethanol,

hydrogenated bisphenol A. If the aliphatic urethane (meth)acrylate is to have self-emulsifying properties in water, corresponding proportions by quantity of low-molecular aliphatic diols and/or polyols having ionic groups, or groups that can be converted into ionic groups, can be used additionally for the synthesis of the aliphatic urethane (meth)acrylate.

5 For example, low-molecular aliphatic diols and/or polyols carrying carboxyl groups, such as dimethylol propionic acid, can be used for example in a proportion by quantity that provides the aliphatic urethane (meth)acrylate with an acid number of 15 to 60 mg KOH/g, as the low-molecular aliphatic diol.

10 Component I of the resin solid of the clear lacquer coating agent and/or sealing coating agent can contain 0 to 25, preferably only 0 to 10 wt.% of the poly- or oligomers different from the aliphatic urethane (meth)acrylates described above, which have radically polymerisable olefinic double bonds, in particular (meth)acryloyl groups in the molecule. Such poly- or oligomers have for example number average molecular masses ( $M_n$ ) in the  
 15 range 500 to 10000, in particular 500 to 3000 and, for example, have an average of 2 to 20, preferably 3 to 10, radically polymerisable olefinic double bonds per molecule. Examples of such poly- or oligomers are corresponding (meth)acryl functional (meth)acryl copolymers, epoxy resin (meth)acrylates, polyester (meth)acrylates, polyether (meth)acrylates, polyurethane (meth)acrylates different from the aliphatic urethane (meth)acrylates of  
 20 component I, unsaturated polyesters, unsaturated polyurethanes or silicon (meth)acrylates. Component I of the resin solid of the clear lacquer coating agent and/or sealing coating agent contains, in particular, no poly- or oligomers with radically polymerisable olefinic double bonds, different from the aliphatic urethane (meth)acrylates described above.

25 The resin solid of the clear lacquer coating agents and/or sealing coating agents can contain as component II, 0 to 30, more preferably 0 to 10 wt.% and even more preferably 0 to 5 wt.% of one or more reactive thinners having radically polymerisable olefinic unsaturated groups with calculated molar masses of less than 500 each. It is particularly preferred, if the selected proportion of reactive thinners in the resin solid is low and in particular if there is  
 30 no reactive thinner in the clear lacquer coating agent and/or sealing coating agent. The reactive thinners of component II are low-molecular compounds, which can be mono-, di- or

polyunsaturated. The reactive thinners can be volatile, slow-evaporating or non-volatile compounds. Examples of reactive thinners are: (meth)acrylic acid and its esters, maleic acid and its semi-esters, vinyl acetate, vinyl ether, substituted vinyl ureas, ethylene- and propylene glycol di(meth)acrylate, 1,3- and 1,4-butanediol di(meth)acrylate, vinyl(meth)acrylate, allyl(meth)acrylate, glycerine tri-, di- and mono(meth)acrylate, trimethylol propane tri-, di- and mono(meth)acrylate, styrene, vinyl toluene, divinyl benzene, pentaerythrite tri-, and tetra(meth)acrylate, di- and tripropylene glycol di(meth)acrylate, hexanediol di(meth)acrylate and mixtures thereof.

- 10 The clear lacquer coating agents and/or sealing coating agents preferably contain photo-initiators e.g. in quantities of 0.1 to 5 wt.% in relation to the resin solid. It is beneficial, if the absorption of the photo-initiators is in the wavelength range of 260 to 450 nm. Examples of photo-initiators are benzoin and derivatives, acetophenone and derivatives, e.g. 2,2-diacetoxyacetophenone, benzophenone and derivatives, thioxanthone and derivatives, anthraquinone, 1-benzoylcyclohexanol, phosphorus-organic compounds, such as e.g. acylphosphine oxides. The photo-initiators can be used alone or in combination. Other synergistic components, e.g. tertiary amines, can also be used.

- 20 The clear lacquer coating agents and/or sealing coating agents used in the process according to the invention can contain thermally activated radical initiators. Examples of thermolabile radical initiators are: organic peroxides, organic azo compounds or C-C splitting initiators, such as dialkyl peroxides, peroxocarboxylic acids, peroxodicarbonates, peroxide esters, hydroperoxides, ketone peroxides, azo dinitriles or benzopinacolsilylether. They are preferably used in quantities of 0.1 to 5 wt.% in relation to the resin solid.

- 25 The clear lacquer coating agents and/or sealing coating agents used in the process according to the invention can contain transparent pigments or fillers and conventional lacquer additives such as e.g. antioxidants, sensitisers, levelling agents, rheology controllers and light protection agents in the conventional quantities for lacquers.

The clear lacquer coating agents and/or sealing coating agents used in the process according to the invention have, for example, a solids content of 25 to 70 wt.%, preferably 30 to 70 wt.%, also preferably 25 to 60 wt.%. As clear lacquer coating agents they preferably have a solids content of 30 to 70 wt.%, as sealing coating agents a solids content of 25 to 60 wt.%.

5

The solid is formed by the resin solid and other non-volatile constituents.

In general, the clear lacquer coating agents are coating agents based on organic solvents.

Their solids content is thus, for example, 45 to 70 wt.%, preferably 50 to 60 wt.%. In

10 In general, the sealing coating agents are also coating agents based on organic solvents. Their solids content is thus 30 to 60 wt.%, preferably 40 to 55 wt.%. Both the clear lacquer coating agents and the sealing coating agents thus contain volatile organic solvents, such as for example glycol ethers, such as butyl glycol, butyl diglycol, dipropyleneglycol dimethylether, dipropyleneglycol monomethylether, ethyleneglycol dimethylether; glycolether esters, such as ethylglycol acetate, butylglycol acetate, 3-methoxy-n-butyl acetate, butyldiglycol acetate, 15 methoxypropyl acetate; esters such as butyl acetate, isobutyl acetate, amyl acetate; ketones such as methylethyl ketone, methylisobutyl ketone, diisobutyl ketone, cyclohexanone, isophorone; alcohols such as methanol, ethanol, propanol, butanol, aromatic hydrocarbons, such as xylene, Solvesso 100 (registered trademark for a mixture of aromatic hydrocarbons with a boiling range of 155 to 185°C) and aliphatic hydrocarbons.

20

The sealing coating agents can also be aqueous coating agents, for example emulsions with a solids content of 25 to 45 wt.%. The clear lacquer coating agents can also be aqueous coating agents, for example with a solids content of 30 to 70 wt.%, for example an emulsion.

25 Here, both the clear lacquer coating agents and the sealing coating agents, are emulsified by the addition of external emulsifiers or are systems containing groups which self-emulsify in water, for example ionic groups. The emulsion systems can also contain organic solvents, in particular water-miscible solvents.

30 In the process according to the invention, the clear lacquer coating agents are applied to colour and/or effect-providing, preferably dried or cured, base lacquer coats previously

applied to substrates. The base lacquer coats can be applied from solvent-based or aqueous base lacquers. The base lacquers contain the usual physically drying and/or chemically crosslinking binders, inorganic and/or organic coloured pigments and/or effect pigments such as e.g. metallic or pearlescent gloss pigments and optionally the conventional lacquer auxiliaries such as e.g. catalysts, levelling agents or anti-pitting agents. These base lacquers are applied either directly to conventional substrates or to pre-coated substrates. Before the base coat is applied the substrates can be provided e.g. with the conventional priming, filling and intermediate coats, such as e.g. are usual for multi-coat lacquers in the motor vehicle sector. Suitable substrates are metal or plastic parts, for example automobile bodywork and bodywork parts. Before further coating with the clear lacquer coating agent, the base lacquer coats are ventilated or preferably dried and optionally chemically cured, for example stoved, in such a way that they contain only small proportions of volatile substances. In particular at the time of the radiation-induced crosslinking reaction by radical polymerisation of the clear lacquer coating layer applied to the base lacquer coat as a top coat, no substantial proportions of volatile constituents should remain in the base lacquer coat. The base lacquer coat can be dried and optionally chemically cured at ambient temperature or temperatures for example up to 150°C. During this process, a chemical crosslinking reaction of the base lacquer coat cannot be ruled out.

The clear lacquer coating agents are applied in a dry coat thickness of preferably 25 to 50µm, for example, to previously applied colour- and/or effect-providing base lacquer coats.

The outer finishing coat of a lacquered surface of a substrate to be provided with a sealing coat by the process according to the invention can be a single-coat finishing lacquer, and is preferably outer finishing lacquer coats or outer clear lacquer coats of multi-coat lacquers, in particular, for example, base lacquer/clear lacquer finishing lacquers, of motor vehicles or motor vehicle parts.

The sealing coats to be applied to the outer finishing coat of lacquered substrate surfaces by the process according to the invention should increase the resistance of the lacquered substrates to scratching, for example scratching from washing or scratching as a result of

wear and tear. They can be applied to the entire visible outer surface of a substrate or only to parts of its surface, in particular areas subject to scratching. Examples of areas of a motor vehicle particularly subject to scratching in use are areas near to locks and door handles and loading edges or door entries, in particular, for example, protruding sills located underneath the door entries, which are particularly subject to scratching during entry and exit. Other examples of areas of a motor vehicle's bodywork subject to scratching are areas suitable for carrying external loads, such as the roof or back of the vehicle.

The sealing coating agents are applied to the outer finishing coat of a lacquered surface of a substrate in a dry coat thickness of, for example, preferably 10 to 30  $\mu\text{m}$ . It may be useful to rub down the lacquered surface to be sealed before applying the sealing coating agent. The clear lacquer and/or sealing coating agent are preferably applied by spraying.

Before curing, the clear lacquer coat and/or sealing coat can optionally be briefly ventilated. It is often useful and preferred to reinforce the ventilation by heating, for example preferably using infra-red radiation. It may be useful to take measures during application and ventilation to prevent, as far as possible, entry of light on a wavelength of less than 380 nm. After the optional ventilation period, the clear lacquer coat and/or sealing coat is subjected to high-energy radiation. This is, for example, electron radiation or preferably ultraviolet radiation. UV radiation sources with emissions in the wavelength range 180 to 420 nm, preferably 200 to 400 nm are preferred. Examples of such UV radiation sources are optionally doped mercury high pressure-, medium pressure- and low pressure radiators, gas discharge tubes such as e.g. xenon low pressure lamps, microwave activated UV radiators, black light tubes, high-energy-electron flash devices such as e.g. UV flash lights.

The UV radiation sources can be designed to operate continuously or discontinuously. A possibility for creating UV sources which can be turned on and off for short periods (pulsing) is to place e.g. mobile screens in front of them or to use UV flash lights.

The arrangement of the radiation sources is known in principle, and can be adapted to the requirements of the substrate and/or the areas of a substrate provided with the un-cured

sealing coat, for example automobile bodywork or parts thereof. For example, the whole substrate can be irradiated, e.g. by passing through a UV irradiation tunnel or a radiation curtain can be used, which moves in relation to the substrate. In addition, an automatic device can be used to pass a point-shaped source of radiation or a small area radiator over  
5 the substrate and/or relevant areas of the substrate.

The distance of the radiation source can be fixed or adapted to a desired value of the substrate shape. The distances of the radiation sources are preferably in the range 2 to 50 cm, in particular 5 to 30 cm from the surface of the un-cured clear lacquer coat or sealing  
10 coat.

Of course the process measures given by way of example can also be combined. This can be done in a single process step or in process steps separated from each other in space or time.

15 The duration of irradiation is, for example, in the range of the duration of a UV flash of, for example, 100 milliseconds to 5 minutes, depending on the irradiation process used and the type and number of UV radiation sources. The duration of radiation, i.e. the time of the actual action of the UV radiation on the un-cured clear lacquer coat or sealing coat is preferably less than 5 minutes.

20 Once the clear lacquer coat and/or sealing coat has been cured, it can be thermally treated by convection, IR and/or NIR irradiation, for example if the clear lacquer coat and/or sealing coat applied consists of a clear lacquer coating agent and/or sealing coating agent containing thermolabile radical initiators.

25 The base lacquer/clear lacquer two-coat lacquers produced by the process according to the invention provide the substrates to which they are applied, for example motor vehicle bodywork or bodywork parts, with resistance to scratching, for example scratching as a result of washing or wear and tear. Examples of areas of a motor vehicle particularly subject  
30 to scratching in use are areas near to locks or door handles and loading edges, door entrances or sills. Other examples of areas of a motor vehicle's bodywork subject to scratching are

areas suitable for carrying external loads, for example the roof or back of the vehicle. The base lacquer/clear lacquer two-coat lacquer finishes are therefore particularly suitable for use as vehicle and vehicle bodywork lacquers.

- 5 No colour and effect deviations in the base lacquer/clear lacquer two-coat lacquers as a result of partial dissolution of the base lacquer after application of the clear lacquer can be observed. The base lacquer/clear lacquer two-coat lacquers and/or sealing coats produced by the process according to the invention are characterised by excellent scratch-resistance and good flexibility.



Examples 1a-1 (Production of urethane acrylates from polyol, polyisocyanate and butane diol monoacrylate (BDMA), general production specification):

According to Table 1, 70 or 80 wt.% solutions of urethane acrylates are produced, by first  
5 dissolving the polyol in the solvent (S) at 65°C. The polyisocyanate is then added at 65°C  
and the batch is heated to 70°C. Once the exothermic reaction is complete, the batch is run at  
80°C until a constant NCO number is established. 0.05 wt.% each, in relation to the total  
batch, of 4-methoxyphenol (inhibitor) and DBTL (catalyst) is then added. BDMA is added  
at 60°C in such a way that the temperature does not rise above 80°C. Once an NCO number  
10 of <0.1 is reached, the solids content is set with solvents (S).

The examples given in Table 1 were carried out by this process.

Table 1

Example	S	1 Mol polyisocyanate	Mol polyol	Mol BDMA	Solids content (wt.%)	Calculated molar mass	Calculated functionality
1a	Butyl acetate	Trimeric HDI	0.25 NPG	2.5	80	1279	3.33
1b	Butyl acetate	Trimeric HDI	0.125 NPG	2.75	80	1122	3.14
1c	Butyl acetate	Trimeric HDI	0.5 NPG	2	80	1826	4
1d	Butyl acetate	Trimeric HDI	0.375 NPG	2.25	80	1498	3.6
1e	o-xylene	Trimeric HDI	0.125 NPG	2.75	80	1122	3.14
1f	o-xylene	Trimeric HDI	0.125 NPG	2.75	70	1230	3.14
1g	o-xylene	Trimeric IPDI	0.125 hexane diol	2.75	70	1232	3.14
1h	o-xylene	Trimeric HDI	0.125 BEPD	2.75	80	1130	3.14
1i	o-xylene	Trimeric HDI	0.125 hexane diol	2.75	80	1124	3.14
1k	o-xylene	Trimeric HDI	0.083 TMP	2.75	80	1176	3.3
1l	o-xylene	HDI biuret	0.125 NPG	2.75	80	1122	3.14
1m	Butyl acetate	Trimeric HDI	∕	3	80	1005	3

## Abbreviations used:

BDMA, butanediol monoacrylate

DBTL, dibutyl tin dilaurate

HDI, hexane diisocyanate

5 IPDI, isophorone diisocyanate

NPG, neopentyl glycol

BEPD, butylethyl propanediol

TMP, trimethylol propane

10 Example 1 n (Production of a urethane acrylate):

A 70% solution of a urethane acrylate is produced, by first dissolving 1.5 mol pentaerythrite triacrylate in butyl acetate at 65°C. Then 1 mol HDI-biuret is added at 65°C and the batch is heated to 70°C. Once the exothermic reaction is complete, the batch is run at 80°C until a

15 constant NCO number is established. 0.05 wt.% each, in relation to the total batch, of 4-methoxyphenol (inhibitor) and DBTL (catalyst) is then added. 1.5 mol BDMA is added at 60°C in such a way that the temperature does not rise above 80°C. Once an NCO number of <0.1 is reached, the solids content is set to 70 wt.% in butyl acetate. The urethane acrylate has a calculated molar mass of 1236 and a calculated functionality of 6.

20

Example 2a-i (Production of clear lacquer coating agents and multi-coat lacquers according to the invention):

The resin solutions from examples 1a-e and 1h-l are each thinned with butyl acetate to a

25 solids content of 60 wt.%. 97 parts by weight of each solution is mixed with 0.1 parts by weight of a radically polymerisable silicon levelling additive, 1 part by weight of a light protection agent (HALS, hindered amine light stabiliser) 0.5 parts by weight of a UV absorber based on benzene triazol, 1 part by weight of a photo-initiator from the alpha hydroxy ketones group and 0.4 parts by weight of a photo-initiator from the acylphosphine

30 oxides group.

The clear lacquer coating agents thus obtained are each applied by spraying in a dry coat thickness of 35  $\mu\text{m}$  to test sheets provided with a three-coat base coating of cathodic dip coat (CDC) primer, filler and base lacquer coat dried for 10 minutes at 80°C. After ventilating for 10 minutes at 60°C the clear lacquer finishing coat is cured by UV radiation (mercury medium-pressure radiator with a capacity of 100 W/cm, distance from object 14 cm, belt speed 1.5 m/min).

Examples 3a-k (Production of sealing coating agents and sealed multi-coat lacquers according to the invention):

The resin solutions from examples 1a to e and 1h-m are each thinned with butyl acetate to a solids content of 40 wt.%. 97 parts by weight of each of these solutions is mixed with 0.1 part by weight of a radically polymerisable silicon levelling additive, 1 part by weight of a light protection agent (HALS, hindered amine light stabiliser), 0.5 parts by weight of a UV absorber based on benzotriazol, 1 part by weight of a photo-initiator from the alpha-hydroxy ketones group and 0.4 parts by weight of a photo-initiator from the acyl phosphine oxides group.

The sealing coating agents thus obtained are each applied by spraying in a dry coat thickness of 20  $\mu\text{m}$  to test sheets provided with a typical four coat automobile lacquer (cathodic dip coat (CDC) primer, filler, base lacquer coat and clear lacquer coat). After ventilating for 5 minutes at 60°C, the sealing coat is cured by UV radiation (mercury medium-pressure radiator with a capacity of 100 W/m, distance from object 14 cm, belt speed 1.5 m/min).

Examples 2 k-m (Production of clear lacquer coating agents and multi-coat lacquers, reference examples):

The procedure is the same as in examples 2a-i, however the resin solutions from examples 1f, g and n are used.

The clear lacquer coating agents 2a-m did not result in partial dissolution of the base lacquer and alteration of the colour.

Table 2 summarises the technological test results for the multi-coat lacquers 2a-m:

5

Multi-coat lacquers	Resin solution from example	Residual gloss (%) <sup>1)</sup>	Elasticity <sup>2)</sup>
Examples according to the invention			
2a	1a	84	4.9
2b	1b	80	5.3
2c	1c	82	5.0
2d	1d	80	5.0
2e	1e	83	5.3
2f	1h	79	5.3
2g	1i	82	5.4
2h	1k	83	5.2
2i	1l	82	5.5
Reference examples			
2k	1f	25	3.6
2l	1g	23	4.3
2m	1n	68	3.2

10

- 1) The residual gloss in % was measured (relationship of initial gloss (20°) of the multi coat lacquer to the gloss after scratching as a result of washing, gloss measured in each case at an illumination angle of 20°). Wash scratching was carried out using a laboratory car wash from Amtec Kistler (cf. Th. Klimmasch and Th. Engbert, Entwicklung einer einheitlichen Laborprüfmethode für die Beurteilung der Waschstraßenbeständigkeit von Automobil-Decklacken [ development of a standard laboratory test method for assessing the resistance to car washes of automobile finishing lacquers] DFO Report Volume 32, pages 59 to 66, Technology Days, volume

of reports from the seminar on 29 and 30/4/1997 in Cologne, published by Deutsche Forschungsgesellschaft für Oberflächenbehandlung e.V. Adersstraße 94, 40215 Düsseldorf).

- 5    <sup>2)</sup>    Indentation to DIN ISO 1520 measured.

Examples 3 l-n (Production of sealing coating agents and sealed multi-coat lacquers, comparative examples):

- 10    The procedure is the same as for examples 3a-k, however the resin solutions from examples 1f, g and n are used.

Table 3 summarises the technological test results for the sealed multi-coat lacquers 3a-n:

Sealed multi coat lacquer	Resin solution from example	Residual gloss (%) <sup>1)</sup>	Elasticity <sup>2)</sup>
Examples according to the invention			
3a	1a	84	5.8
3b	1b	80	6.2
3c	1m	80	6.3
3d	1c	82	5.5
3e	1d	80	5.8
3f	1e	83	6.0
3g	1g	79	6.1
3h	1i	82	6.0
3i	1k	83	5.9
3k	1l	82	6.0
Reference examples:			
3l	1f	25	4.5
3m	1g	23	6.0
3n	1n	68	3.8

- 1) The residual gloss in % (relationship between initial gloss (20°) of the sealed multi-coat lacquer and the gloss after scratching as a result of washing, gloss measured in each case at an illumination angle of 20°). The wash scratching was carried out using a laboratory car wash from Amtec Kistler (cf. Th. Klimmasch and Th. Engbert, Entwicklung einer einheitlichen Laborprüfmethode für die Beurteilung der Waschstraßenbeständigkeit von Automobil-Decklacken [ development of a standard laboratory test method for assessing the resistance to car washes of automobile finishing lacquers] DFO Report Volume 32, pages 59 to 66, Technology Days, volume of reports from the seminar on 29 and 30/4/1997 in Cologne, published by Deutsche.

Forschungsgesellschaft für Oberflächenbehandlung e.V. Adersstraße 94, 40215  
Düsseldorf).

- 2) Indentation according to DIN ISO 1520 was measured.



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E. I. du Pont de Nemours and Company

Claims:

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1. Process for the production of a base lacquer/clear lacquer two-coat lacquer system and/or a transparent sealing coat on the outer finishing coat of a lacquered surface of a substrate, in which a clear lacquer coat cured by radical polymerisation is applied to a previously applied colour- and/or effect-providing base lacquer coat and/or a transparent coating agent cured by radical polymerisation is applied to the lacquered surface of a substrate and cured by the action of high-energy radiation, characterised in that a transparent coating agent is used to apply the outer clear lacquer coat and/or sealing coat, of which the resin solid consists of:

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- I. 70 to 100 wt.% of one or more radically polymerisable oligo- and/or prepolymers containing olefinically unsaturated groups and
- II. 0 to 30 wt.% one or more radically polymerisable reactive thinners having olefinically unsaturated groups with calculated molar masses of less than 500 each,

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wherein 75 to 100 wt.% of component I is an aliphatic urethane (meth)acrylate with an average (meth)acryloyl functionality of 3 to 4.5 per molecule and a calculated molecular mass of at least 826, which can be obtained by reacting acyclic aliphatic diisocyanates with 8 C atoms and/or polyisocyanates derived from such diisocyanates with one or more low-molecular aliphatic compounds, which have one or more hydroxy groups and at the same time one or more (meth)acryloyl groups, and optionally with one or more low-molecular aliphatic diols and/or polyols.

2. Process according to claim 1, characterised in that the resin solid of the transparent coating agent consists of:
  - I. 90 to 100wt.% of one or more radically polymerisable oligo- and/or prepolymers containing olefinically unsaturated groups and
  - II. 0 to 10 wt.% of one or more radically polymerisable reactive thinners containing olefinically unsaturated groups with calculated molar masses of less than 500 each.
3. Process according to claim 1 or 2, characterised in that methyl pentane diisocyanate (MPDI) and/or hexane diisocyanate (HDI) are used as acyclic aliphatic diisocyanates with 8 C atoms and polyisocyanates with carbodiimide groups, allophanate groups, isocyanurate groups, uretdione groups and/or biuret groups are used as the polyisocyanates derived from them.
4. Process according to claim 3, characterised in that tris-(6-isocyanatohexyl)-biuret and/or the isocyanurate derived from HDI is used as the polyisocyanate.
5. Process for the production of a sealing coat according to one of claims 1 to 4, characterised in that the transparent sealing coat is applied to a single-coat finishing lacquer coat or to the outer finishing lacquer coat or outer clear lacquer coat of multi-coat lacquers.
6. Process according to any one of claims 1 to 5, characterised in that it is used for lacquering and/or sealing motor vehicles or motor vehicle parts.
7. Process according to any one of claims 1 to 6, characterised in that the sealing coat is applied to areas of the surface of a lacquered substrate that are particularly subject to scratching.

8. Process according to claim 7, characterised in that the sealing coat is applied to areas near the locks, door handles, door entrances, loading edges, roof and/or back of a motor vehicle.
- 5 9. Substrate, lacquered according to the process of any one of claims 1 to 8.

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E. I. du Pont de Nemours and Company

**Abstract:**

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Process for the production of a base lacquer/clear lacquer two-coat lacquer and/or a transparent sealing coat on the outer finishing coat of a lacquered surface of a substrate by application of a transparent coating agent cured by radical polymerisation and curing by the action of high-energy radiation, a transparent coating agent being used, of which the resin solid consists of:

10

I. 70 to 100 wt.% radically polymerisable oligo- and/or prepolymers having olefinic groups

II. 0 to 30 wt.% radically polymerisable reactive thinners having olefinic groups, with calculated molar masses of less than 500 each,

15

wherein 75 to 100 wt.% of component I is an aliphatic urethane (meth)acrylate with an average (meth)acryloyl functionality of 3 to 4.5 per molecule and a calculated molecular mass of at least 826, which can be obtained by reacting acyclic aliphatic diisocyanates with 8 C atoms and/or polyisocyanates derived from such diisocyanates with low-molecular aliphatic compounds, which have one or more hydroxyl groups and at the same time one or

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more (meth)acryloyl groups.

## DECLARATION and POWER OF ATTORNEY

FA-10608

As a below-named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

Method for producing base varnish/clear varnish-two-coat varnishes and/or transparent sealing layers

the specification of which is attached hereto unless the following box is checked:

☒ I was filed on 26.09.2000 as U.S. Application No. \_\_\_\_\_ or PCT International Application No. EP00/09387 and was

amended on \_\_\_\_\_ (if applicable).

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is known to me to be material to patentability as defined in 37 CFR § 1.56.

I hereby claim foreign priority benefits under 35 U.S.C. § 119(a)-(d) or § 365(b) of any foreign application(s) for patent or inventor's certificate, or § 365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or PCT International application having a filing date before that of the application on which priority is claimed.

Application No.	Country	Filing Date	Priority Claimed (Yes/No)
199 47 433.8 / 199 56 659.3	DE/DE	02.10.1999/25.11.1999	yes/yes

I hereby claim the benefit under 35 U.S.C. § 119(e) of any United States Provisional Application(s) listed below.

U.S. Provisional Application No.

U.S. Filing Date

I hereby claim the benefit under 35 U.S.C. § 120 of any United States application(s), or § 365(c) of any PCT International Application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application or PCT International Application in the manner provided by the first paragraph of 35 U.S.C. § 112, I acknowledge the duty to disclose information which is known to me to be material to patentability as defined in 37 CFR § 1.56 which became available between the filing date of the prior application and the national or PCT International filing date of this application.

Application No.	Filing Date	Status (patented, pending or abandoned)
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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

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1433-5744 UNPOTFA 1068

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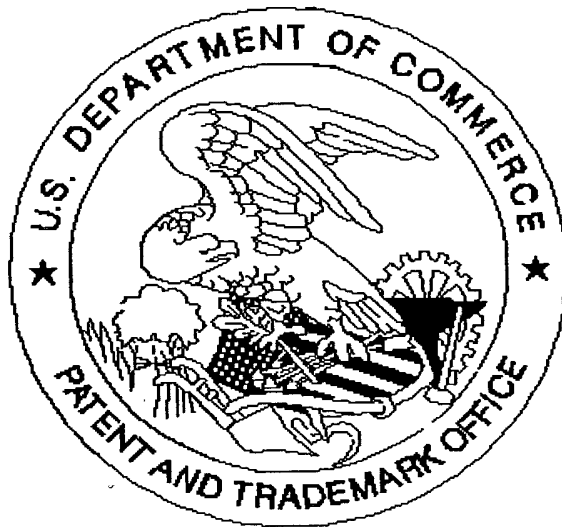
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